

FRACTIONATION OF THE ORGANIC BASES
DERIVED FROM CEREBROSIDES

BY

OLGA NALBANDOV

B.S., Oklahoma A. and M. College, 1935

M.S., Oklahoma A. and M. College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

When cerebrosides are hydrolyzed by sulfuric acid in methanol a small amount of O-methylsphingosine is formed (1,2,3). Rosenheim (4) has suggested that this compound arises during the splitting of the galactoside bond. This explanation does not seem satisfactory for hydrolysis of glycosides with methanolic acid leads to the formation of the methyl glycoside rather than the methyl ether of the aglucon.

Carter and associates (5) have shown recently that sphingosine is 1,3-dihydroxy-2-aminooctadecene-4. With a double bond in the 4,5-position and a hydroxyl group on carbon number three the substance is an allylic alcohol. Such an alcohol might be expected to give rise to small amounts of the methyl ether when refluxed with methanolic sulfuric acid. If this explanation of the formation of O-methylsphingosine is correct the location of the methoxyl group would be carbon number three in the molecule.

In order to establish the location of the methoxyl group of O-methylsphingosine periodic acid oxidation of dihydro-O-methylsphingosine was undertaken. If the methoxyl group is located on carbon number three the products of periodic oxidation of the molecule should be one mole of α -methoxymargaraldehyde, one mole of formaldehyde, and one mole of ammonia. The other possible structure of the ether is that in which the methoxyl group is attached to carbon number one. If this is the correct structure periodic acid oxidation of dihydro-O-methylsphingosine should yield one mole each of palmitaldehyde, methoxycetaldehyde, and ammonia.

To carry out this investigation it was necessary to devise a method for complete separation of O-methylsphingosine

from the other basic constituents of the sphingolipid hydrolysate.

DISCUSSION OF RESULTS

Sphingosine p-hydroxyazobenzene-p'-sulfonate was found to be more soluble in methyl alcohol than the corresponding salts of dihydrosphingosine and O-methylsphingosine. The sulfonates of the latter two bases are similar in solubilities but the sulfates of these two bases differ widely in their solubility in methanol, dihydrosphingosine sulfate being almost insoluble at room temperature whereas O-methylsphingosine sulfate is very soluble. Cleancut separation of the three bases was achieved by converting the mixture of bases to the sulfates and removing the methanol-insoluble sulfate fraction. The mixture of bases recovered from the methanol-soluble fraction was converted to the p-hydroxyazobenzene-p'-sulfonates in methanol. The least soluble salt was removed and pure O-methylsphingosine recovered from it. The methanol-insoluble sulfate fraction was converted to the p-hydroxyazobenzene-p'-sulfonate. The sulfonate fraction which was least soluble in methanol was removed and dihydrosphingosine was obtained from it. Sphingosine was obtained from the methanol-soluble p-hydroxyazobenzene-p'-sulfonate fraction.

O-Methylsphingosine was reduced catalytically and the dihydro base was subjected to periodic acid oxidation. From the products of the reaction one mole of formaldehyde per mole of dihydro-O-methylsphingosine was isolated as the dimedon derivative, indicating that O-methylsphingosine is 1-hydroxy-2-amino-3-methoxyoctadecene-4.

SUMMARY

A scheme has been devised for the separation of sphingosine, dihydrosphingosine, and O-methylsphingosine in pure form from the products of methanolic sulfuric acid hydrolysis

of sphingolipids.

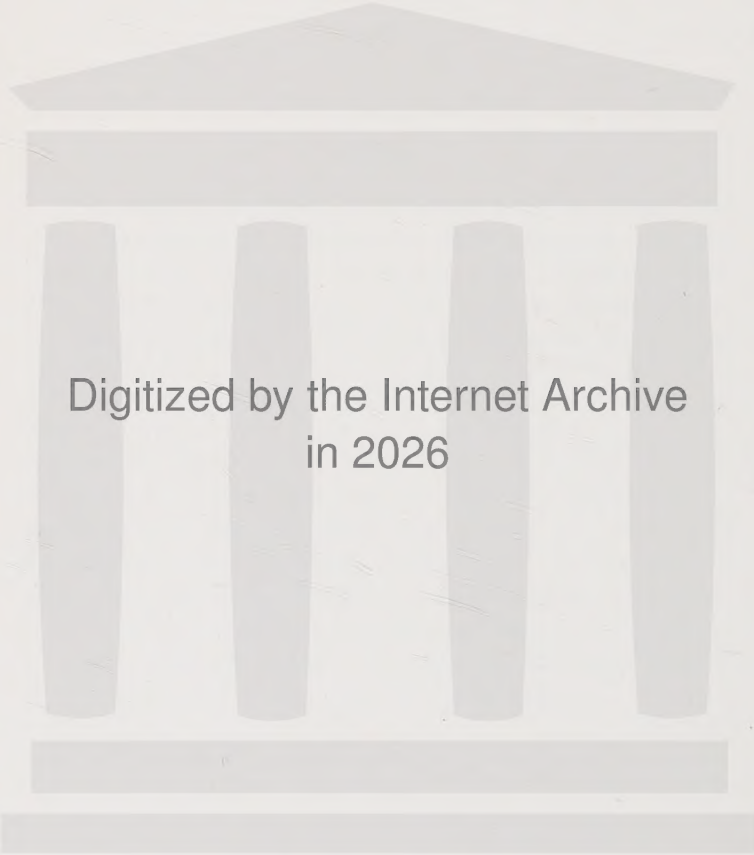
Dihydro-O-methylsphingosine has been shown to yield one mole of formaldehyde on oxidation with periodic acid, indicating that O-methylsphingosine is 1-hydroxy-2-amino-3-methoxyoctadecene-4.

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VITA

The author, née Olga Oliver, was born November 30, 1914, in Marshall, Oklahoma. She attended Russell High School, Durant, Oklahoma, and Sulphur High School, Sulphur, Oklahoma. Her undergraduate training was received at William Woods College (1929-1931) and Oklahoma A. and M. College (1933-1935). She received the degree of Bachelor of Science from the latter institution in 1935, and the Master of Science degree in 1937. In 1935 she married Andrew Nalbandov. From 1937 to 1940 she was employed as technician in the chemistry laboratory of Wisconsin General Hospital, Madison, Wisconsin. In the fall of 1943 she entered the Graduate School of the University of Illinois where she held a teaching assistantship from October, 1943, to June, 1944, and a Graduate School Fellowship from June, 1944, to June, 1945.



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